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Correlation between Ground State Conformation and Excited State Dynamics in a Multichromophoric Dendrimer Studied by Excitation Wavelength Dependent Fluorescence Upconversion

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A time-resolved fluorescence upconversion study on a polyphenylene dendrimer with 16 peryleneimide chromophores at the rim, in which the excitation wavelength is systematically varied while the detection wavelength is kept constant, is reported. A new setup is described which allows excitation at wavelengths as short as 320 nm and throughout the visible range up to 900 nm with a system prompt response on the order of 300 fs. In addition to results reported previously[13] which were obtained at shorter wavelengths indicating the initial formation of a locally excited state which then evolves further into a locally excited state on a 5 ps time scale, the newly obtained data at longer wavelength excitation show the existence of a ground state interaction leading under these conditions of excitation predominantly to a directly formed complex.

Introduction

Dendrimers are highly branched macromolecular systems whose structure can be defined on a molecular level[1,2] and as such have been attracting a lot of attention not only from the synthetic point of view[3] but also from the point of view of their physical and chemical properties.[4−8]

Recently, dendrimers consisting of a polyphenylene core and decorated with peryleneimide chromophores at the rim have been prepared using a novel synthetic approach.[9] Within the research group, these molecules have been chosen for single molecule spectroscopy,[10,11] because they allow topographic and optical observation to be combined on a single molecule level. To understand the dynamics of single molecule spectroscopy, it is essential to evaluate the photophysical processes at the ensemble level. Furthermore, these dendrimers have a high shape persistence, and through synthesis[11] one can control the number of the peryleneimide chromophores.

In a separate publication,[12] a comparative study of three generations of the polyphenylene dendrimers and a model compound using single photon timing will be reported. It was found that all dendrimers show a three exponential decay with similar decay times of the order of 350 ps, 3−4 ns, and 7−8 ns, while the model compound showed a monoexponential decay with a time constant of 4 ns. The longest decay time of the dendrimers was attributed to a decay of an excimer-like entity. Using fluorescence upconversion[13] and anisotropy transient absorption measurements on the second generation of this dendrimer family,[14] an additional faster decay time of 5 ps was found. It was shown that upon excitation with 500 nm light a locally excited state was formed prior to the formation of the complex. The dendrimer was further characterized by a high positive amplitude of the fast fluorescence decay component in the wavelength range between 560 and 600 nm, while the model compound was found to decay in this wavelength range only on a nanosecond time scale. It was, thus, suggested that this 5 ps decay time is associated with the evolution into an excited state, which is delocalized between two or more chromophores in an excimer-like complex. This suggestion was verified for the second generation dendrimer by the observation of a growing in component upon excitation at 500 nm and detection at 620 nm.[13] Nevertheless, the question if and to what extent this complex is already preformed in the ground state was not answered.

In the present contribution, femtosecond time-resolved fluorescence excitation spectroscopy is used to study the correlation between the excited state dynamics and the ground state configuration of a multichromophoric dendrimer. In this approach, the detection wavelength is kept constant, while the wavelength used for the excitation is systematically tuned. This methodology was first reported by Glasbeek et al.[15] In analogy to steady state excitation conditions, where this kind of spectroscopy is well established, applying this together with femtosecond time resolution yields additional and more detailed information about the correlation between the ground state configuration and the excited state kinetics. The third generation of the polyphenylene core dendrimer decorated with 16 peryleneimide chromophores at the rim (**1**, Scheme 1) is compared to a model compound (**2**) in which a hexaphenylbenzene unit is attached to a peryleneimide. Furthermore, the setup that combines an optical parametric amplifier (OPA) as the excitation source and fluorescence upconversion as detection is described in detail.

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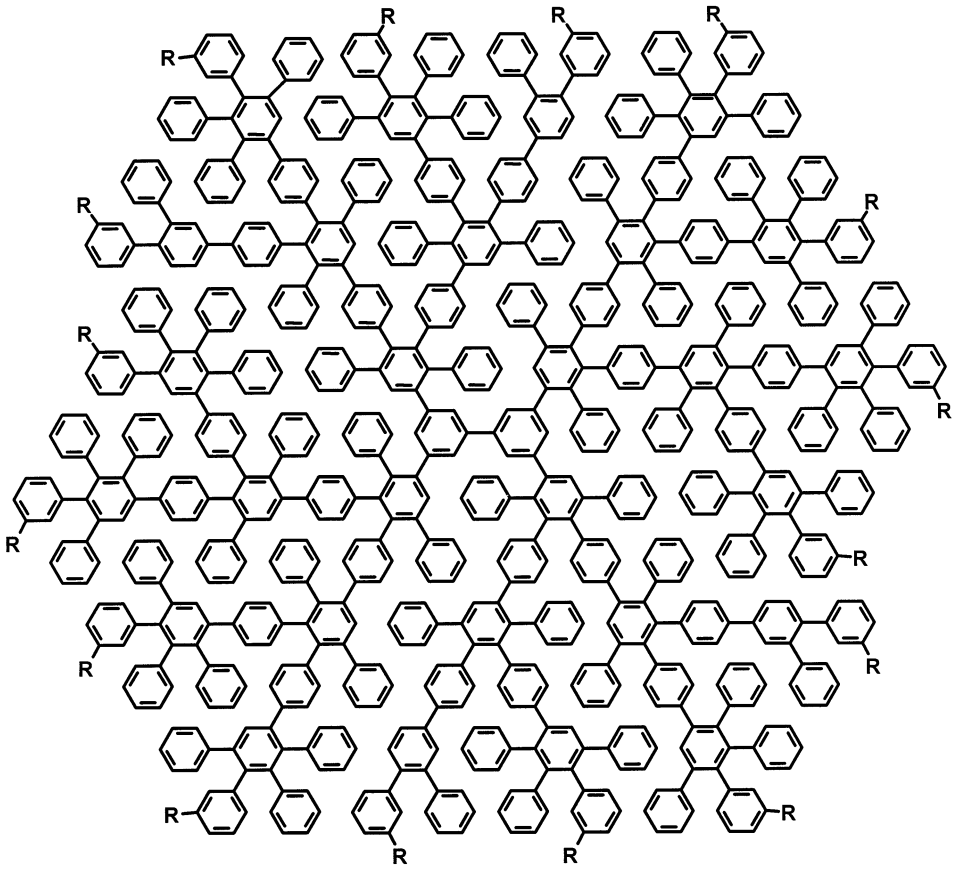
SCHEME 1: Molecular Structure of the Third Generation Polyphenylene Dendrimer 1 and the Model Compound Hexaphenylbenzene Peryleneimide 2



Experimental Section

The laser source has previously been described in detail.[16] In brief, a Nd:YVO_4 laser (Millennia V, Spectra Physics) is used to pump a Ti:sapphire laser (Tsunami, Spectra Physics). Its output seeds a regenerative amplifier (RGA, Spitfire, Spectra Physics). The output of the RGA (1 mJ, 100 fs, 800 nm) is split in two equal parts, one of which is used to pump an optical parametric generator/amplifier (OPA-800, Spectra Physics). The output wavelength range of the OPA is extended by harmonic generation using one or two BBO crystals, thus making a range of 300−900 nm accessible.

The experimental setup is shown in detail in Figure 1. The output of the OPA is passed through a multichromatic half wave plate (Berek compensator, New Focus 5540) and focused onto the sample using a 200 mm lens. The fluorescence is then collected by means of a 10× microscope objective lens (M-10x, Newport) and focused by a 150 mm lens into an appropriate crystal with nonlinear optical properties. The cross correlation measured between the excitation and gate pulses had a width of 180 fs (full width at half-maximum, fwhm). Besides this, the overall temporal resolution of our setup is limited by the angle α (refer to Figure 1) between the excitation beam and the collected fluorescence light. Using an angle of 10°, a temporal resolution of 260 fs at a wavelength of 500 nm could be achieved.

The second part of the RGA output is sent into a variable delay line and focused by a 750 mm lens, the focal plane of which was selected to be 100 mm behind the nonlinear crystal (LBO, 1 mm). The angle β between this gate beam and the collected fluorescence was set to 7°, which was selected in order to allow for easy spatial filtering of the upconversion signal while still keeping a high conversion efficiency and good temporal resolution.

The generated sum frequency light was then collimated (300 mm) and focused (150 mm) using UV-coated fused silica lenses (Newport) into the entrance slit of a 300 mm focal length monochromator (Acton Research Corp. 300-I, 600 lines/mm gratings blazed at 300 and 500 nm). The signal passing through the output slit was detected by a UV-sensitive photomultiplier

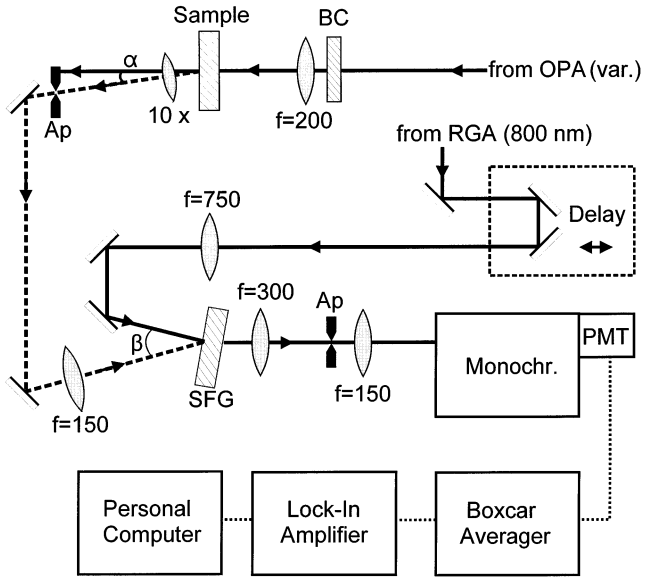


Figure 1. Experimental setup (schematic): OPA, optical parametric amplifier; AP, aperture; SFG, nonlinear optical crystal for sum frequency generation; BC, Berek Compensator; PMT, photomultiplier tube.

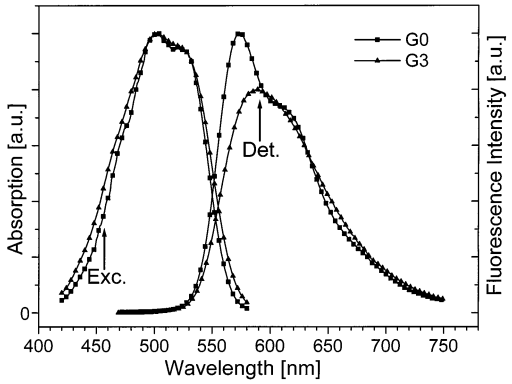


Figure 2. Excitation and emission spectra of **1** (▲) and **2** (■) in chloroform at room temperature. Excitation spectra were detected at 590 nm, fluorescence spectra were excited at 460 nm.

tube (R1527p, Hamamatsu). The electrical signal from the photomultiplier tube was gated by a boxcar averager (SR 250, Stanford Research Systems), and the phase sensitivity was detected by a lock-in amplifier (SR 830, Stanford Research Systems). This scheme proved to be essential for the detection of fluorescence upconversion signals up to and at 700 nm, as at those wavelengths various nonlinear processes generate a significant amount of additional light. The temporal response function of the system is shown (IRF) in Figure 3, which was determined by measuring the upconversion of light scattered from the sample.

Results and Discussion

The steady-state excitation and fluorescence spectra of **1** and **2** in chloroform at room temperature are shown in Figure 2. The excitation spectrum of **1** is similar to that of the model compound. The fluorescence spectra show more drastic differences; the spectrum of **2** has a maximum at 574 nm and a shoulder at 600 nm, while the spectrum of **1** is structureless and its maximum is shifted to the red by 1450 cm^{-1}. The excitation and fluorescence spectra as well as the quantum yield

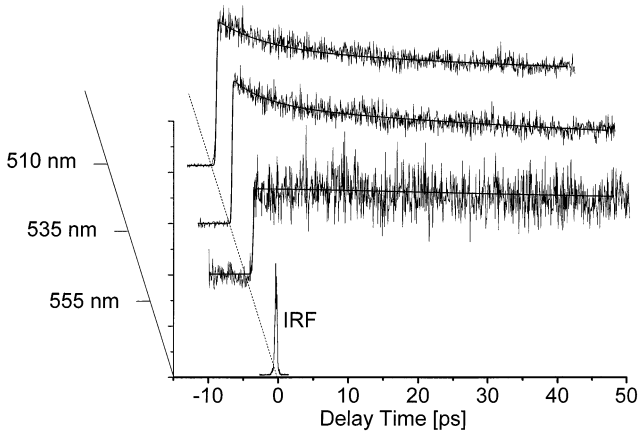


Figure 3. Fluorescence decay curves of **1**. The detection of the fluorescence was at 590 nm, while the excitation was made at 510, 535, and 555 nm. The solid lines are the corresponding fits, and IRF is the system prompt response.

of the third generation of the dendrimer **1** are identical to that of the second generation, which was reported previously.[14]

Upconversion measurements of the fluorescence decay were taken in two time windows of 50 and 420 ps. Figure 3 shows fluorescence upconversion decay curves of **1** which were excited at various wavelengths along with the corresponding fits. The detection wavelength was set at 590 nm in all cases.

The fluorescence decay curves of the dendrimer **1** and the model compound **2** could be fitted by a function that was the result of convolution of the instrument response function with sets of exponentials decay function of the form

$$\Phi(t,\lambda) = \sum_i A_i(\lambda) \exp(-t/\tau_i) \qquad (1)$$

The fluorescence of **2** at 590 nm decays monoexponentially on a nanosecond time scale as reported previously.[13,14] The data obtained for the dendrimer **1** could be fitted using a sum of three exponentials resulting in decay times of $\tau_1 = 5$ ps, $\tau_2 =$ 100 ps, and a few nanoseconds; the latter could not be determined exactly using upconversion in view of the data window limitation to 420 ps. The relative contribution to the total amplitude of the picosecond and nanosecond component at 535 nm were 0.4 and 0.6, respectively. A similar distribution was found in SPC[12] for the picosecond and nanosecond components. From previously measured SPT data, it is known that the decay on the nanosecond time scale is biexponential, with a longer decay component that was attributed to a decay of an excimer-like entity.[12] Decay times of the same order of magnitude as τ_1 and τ_2 were found in fluorescence decay measurements of the second generation dendrimer.[13] The values obtained for the third generation are tentatively attributed to similar processes. In particular, it is assumed that the fast decay component is related to the evolution from a locally excited chromophore to an excimer-like complex.[13] In Figure 4, the normalized relative amplitudes $A_i^r = A_i/\sum_i A_i$ are depicted as a function of the excitation wavelength. The values for A_1^r and A_3^r are almost constant in the excitation wavelength range between 465 and 525 nm, but at longer excitation wavelengths A_1^r decreases, becoming zero at 555 nm, while A_3^r increases correspondingly. The relative amplitudes that are associated with the 100 ps decay component are almost constant over the whole excitation range. From SPT measurements reported separately,[12] it is known that upon excitation of **1** at 560 nm the relative amplitude of the long decay component that was attributed to

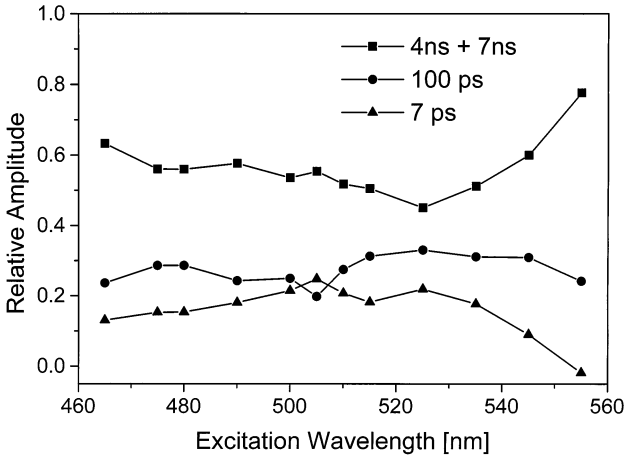


Figure 4. Relative amplitudes of the 5 ps (triangles), 100 ps (circles), and nanoseconds (squares) decay components plotted as a function of the excitation wavelength, measured in chloroform at room temperature.

a decay of a complex is the largest. Therefore, the correlation between the increase of the relative amplitude A_3^r and the decrease of the relative amplitude A_1^r substantiates the assumption that this component is related to the formation of an excimer-like complex in the excited state. Moreover, it can be deduced that at longer wavelengths the excitation is preferentially directly into the complex, which exists already in the ground state, while at shorter wavelengths excitation initially results to a large extent in a locally excited chromophore. Similar results were found in upconversion fluorescence measurements, where at longer detection wavelengths an increase of the amplitude of the long component was also observed.[13]

Conclusions

A new setup that combines the possibility of femtosecond excitation over the wavelength range from 300 to 900 nm with fluorescence upconversion detection was introduced. In particular, this combination allows time-resolved femtosecond excitation spectroscopy, which gives new sets of information on the correlation between the ground state conformation and the excited state processes in a multichromophoric dendrimer. It was found that upon irradiation at shorter wavelengths also a locally excited state is formed initially, which then evolves into an excited state complex. Excitation at longer wavelengths preferentially yields direct formation of an excited complex.

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